

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 08 June 2000 (08.06.00)	
<b>International application No.</b> PCT/US99/25106	<b>Applicant's or agent's file reference</b> PE0612 PCT
<b>International filing date (day/month/year)</b> 26 October 1999 (26.10.99)	<b>Priority date (day/month/year)</b> 27 October 1998 (27.10.98)
<b>Applicant</b> SCHADT, Frank, Leonard, III et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
28 April 2000 (28.04.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

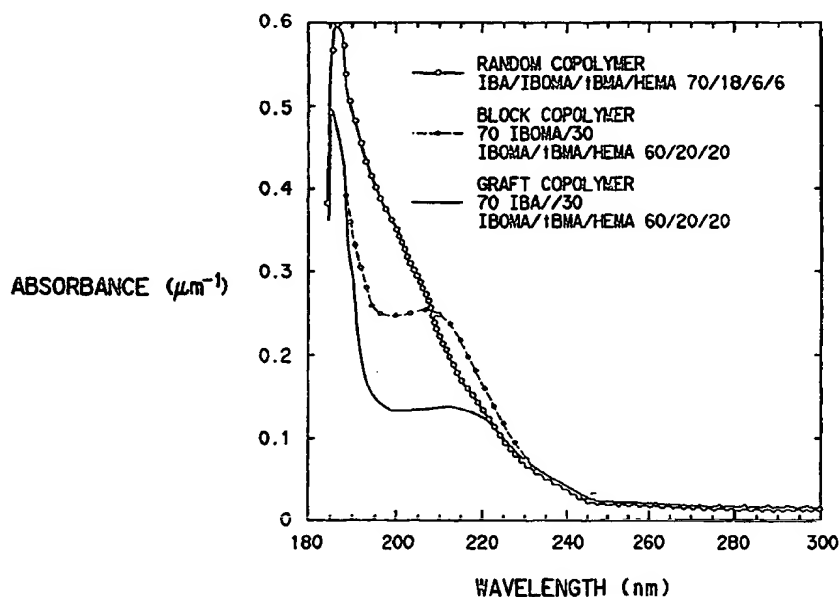
<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer</p> <p>Claudio Borton</p> <p>Telephone No.: (41-22) 338.83.38</p>
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : G03F 7/039, 7/004		A3	(11) International Publication Number: WO 00/25178
			(43) International Publication Date: 4 May 2000 (04.05.00)
(21) International Application Number: PCT/US99/25106 (22) International Filing Date: 26 October 1999 (26.10.99) (30) Priority Data: 60/105,789 27 October 1998 (27.10.98) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SCHADT, Frank, Leonard, III [US/US]; 2407 Delaware Avenue, Wilmington, DE 19806 (US). FRYD, Michael [US/US]; 50 East Maple Avenue, Moorestown, NJ 08057 (US). PERIYASAMY, Mookkan [US/US]; 2623 Pennington Drive, Wilmington, DE 19810 (US). (74) Agent: MAGEE, Thomas, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).			(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, DM, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  Published With international search report.  (88) Date of publication of the international search report: 5 October 2000 (05.10.00)

(54) Title: PHOTORESISTS AND PROCESSES FOR MICROLITHOGRAPHY



## (57) Abstract

Positive photoresists and associated processes for microlithography in the ultraviolet (UV) and violet are disclosed. The photoresists comprise (a) a branched polymer containing protected acid groups and (b) at least one photoacid generator. The photoresists have high transparency throughout the UV, good development properties, high plasma etch resistance and other desirable properties, and are useful for microlithography in the near, far, and extreme UV, particularly at wavelengths less than or equal to 365 nm.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/25106

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 G03F7/039 G03F7/004

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>YAMANA M ; ITANI T ; YOSHINO H ; HASHIMOTO S ; TANABE H ; KASAMA K: "Deblocking reaction of chemically amplified ArF positive" PROC. SPIE - INT. SOC. OPT. ENG., vol. 3333, no. 1, June 1998 (1998-06), pages 32-42, XP002130419 Washington, USA page 33 page 37; figure 1</p> <p style="text-align: center;">--- -/--</p>	1-4,9, 10,27-29

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

29 June 2000

Date of mailing of the international search report

07. 07. 2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Dupart, J.-M.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/25106

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199815 Derwent Publications Ltd., London, GB; Class A89, AN 1998-164829 XP002130420 & JP 10 031310 A (NIPPON GOSEI GOMU KK), 3 February 1998 (1998-02-03) abstract ---	1-4,10, 27-29
X	EP 0 789 278 A (JAPAN SYNTHETIC RUBBER CO.,LTD.) 13 August 1997 (1997-08-13) page 43; examples 7,8 ---	1-4,10, 27-29
A	EP 0 473 547 A (CIBA-GEIGY AG) 4 March 1992 (1992-03-04) claims 6,9-11 ---	5-8
A	EP 0 773 478 A (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 14 May 1997 (1997-05-14) page 13, line 1 - line 50 claim 16 -----	5-8

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 99/25106

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-4, 9-29

A positive-working photoresist comprising:

- (A) a branched polymer containing protected acids, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment; and
- (B) at least one photoacid generator

2. Claims: 5-8

A positive-working photoresist comprising a branched polymer containing (a) protected acids, (b) one or more branch segment(s) chemically linked along a linear backbone segment, and (c) a photoacid generator covalently bonded to the branched polymer.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/25106

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10031310 A	03-02-1998	NONE	
EP 0789278 A	13-08-1997	JP 10111569 A	28-04-1998
EP 0473547 A	04-03-1992	CA 2049772 A	28-02-1992
		JP 4230645 A	19-08-1992
EP 0773478 A	14-05-1997	EP 0877295 A	11-11-1998
		JP 9189998 A	22-07-1997
		US 5928840 A	27-07-1999

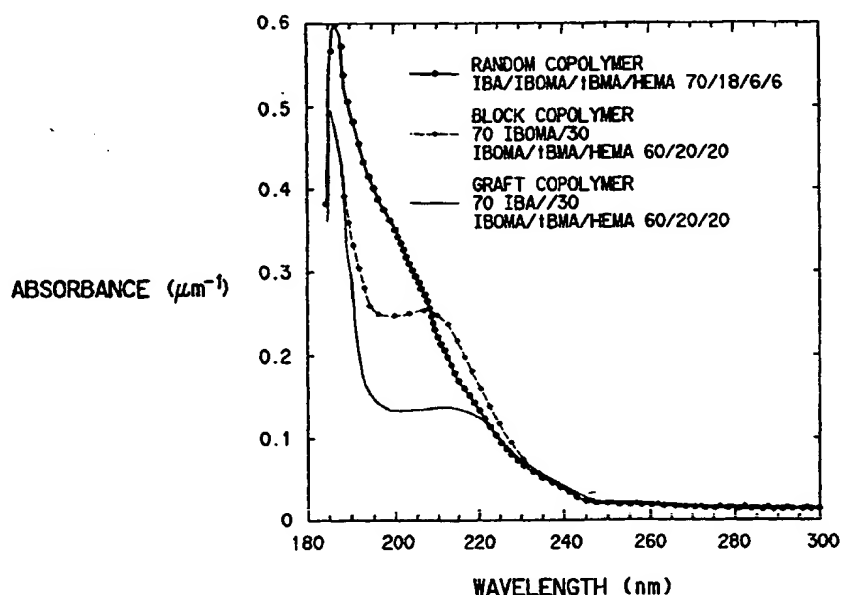




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>G03F 7/</b>	<b>A2</b>	(11) International Publication Number: <b>WO 00/25178</b> (43) International Publication Date: 4 May 2000 (04.05.00)
<p>(21) International Application Number: PCT/US99/25106</p> <p>(22) International Filing Date: 26 October 1999 (26.10.99)</p> <p>(30) Priority Data: 60/105,789 27 October 1998 (27.10.98) US</p> <p>(71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): SCHADT, Frank, Leonard, III [US/US]; 2407 Delaware Avenue, Wilmington, DE 19806 (US). FRYD, Michael [US/US]; 50 East Maple Avenue, Moorestown, NJ 08057 (US). PERIYASAMY, Mookkan [US/US]; 2623 Pennington Drive, Wilmington, DE 19810 (US).</p> <p>(74) Agent: MAGEE, Thomas, H.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, DM, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> Without international search report and to be republished upon receipt of that report.</p>

(54) Title: PHOTORESISTS AND PROCESSES FOR MICROLITHOGRAPHY



## (57) Abstract

Positive photoresists and associated processes for microlithography in the ultraviolet (UV) and violet are disclosed. The photoresists comprise (a) a branched polymer containing protected acid groups and (b) at least one photoacid generator. The photoresists have high transparency throughout the UV, good development properties, high plasma etch resistance and other desirable properties, and are useful for microlithography in the near, far, and extreme UV, particularly at wavelengths less than or equal to 365 nm.

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# PATENT COOPERATION TREATY

2/14/00

From the INTERNATIONAL SEARCHING AUTHORITY

## PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

**RECEIVED**

To:  
E.I. DU PONT DE NEMOURS AND COMPANY  
Legal/Patent Records Center  
Attn. MAGEE, Thomas H.  
1007 Market Street  
Wilmington, Delaware 19898  
UNITED STATES OF AMERICA

**RECEIVED**  
*[Signature]*  
7-2000  
T. H. MAGEE

(PCT Rule 44.1) JUL 10 2000

PATENT RECORDS  
CENTER

Date of mailing  
(day/month/year) 07/07/2000

Applicant's or agent's file reference  
PE0612 PCT

**FOR FURTHER ACTION** See paragraphs 1 and 4 below

International application No.  
PCT/US 99/ 25106

International filing date  
(day/month/year) 26/10/1999

Applicant

E.I. DU PONT DE NEMOURS AND COMPANY et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

**Filing of amendments and statement under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

**Where?** Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after 18 months from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Nathalie Ostwinkel

**TRB NOTED**

## NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

### INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

#### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

#### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

#### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

#### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

**The amendments must be made in the language in which the international application is to be published.**

#### What documents must/may accompany the amendments?

##### Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

**The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.**

## NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

**The following examples illustrate the manner in which amendments must be explained in the accompanying letter:**

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

### **"Statement under article 19(1)" (Rule 46.4)**

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

**It must be in the language in which the international application is to be published.**

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

### **Consequence if a demand for international preliminary examination has already been filed**

If, at the time of filing any amendments and any accompanying statement, under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the time of filing the amendments (and any statement) with the International Bureau, also file with the International Preliminary Examining Authority a copy of such amendments (and of any statement) and, where required, a translation of such amendments for the procedure before that Authority (see Rules 55.3(a) and 62.2, first sentence). For further information, see the Notes to the demand form (PCT/IPEA/401).

### **Consequence with regard to translation of the international application for entry into the national phase**

The applicant's attention is drawn to the fact that, upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>PE0612 PCT</b>	<b>FOR FURTHER ACTION</b> <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. <b>PCT/US 99/ 25106</b>	International filing date (day/month/year) <b>26/10/1999</b>	(Earliest) Priority Date (day/month/year) <b>27/10/1998</b>
Applicant <b>E.I. DU PONT DE NEMOURS AND COMPANY et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 5 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

#### 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☒ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

01

☐ None of the figures.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 99/25106

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

**1. Claims: 1-4, 9-29**

A positive-working photoresist comprising:  
(A) a branched polymer containing protected acids, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment; and  
(B) at least one photoacid generator

**2. Claims: 5-8**

A positive-working photoresist comprising a branched polymer containing (a) protected acids, (b) one or more branch segment(s) chemically linked along a linear backbone segment, and (c) a photoacid generator covalently bonded to the branched polymer



## INTERNATIONAL SEARCH REPORT

PE-0612

International Application No

PCT/US 99/25106

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03F7/039 G03F7/004

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YAMANA M ; ITANI T ; YOSHINO H ; HASHIMOTO S ; TANABE H ; KASAMA K: "Deblocking reaction of chemically amplified ArF positive" PROC. SPIE - INT. SOC. OPT. ENG., vol. 3333, no. 1, June 1998 (1998-06), pages 32-42, XP002130419 Washington, USA page 33 page 37; figure 1 --- -/--	1-4, 9, 10, 27-29

RECEIVED  
AUG 7 - 2000  
T. H. MAGEE☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

29 June 2000

Date of mailing of the international search report

07. 07. 2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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Authorized officer

Dupart, J.-M.

## INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/US 99/25106

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199815 Derwent Publications Ltd., London, GB; Class A89, AN 1998-164829 XP002130420 & JP 10 031310 A (NIPPON GOSEI GOMU KK), 3 February 1998 (1998-02-03) abstract ---	1-4,10, 27-29
X	EP 0 789 278 A (JAPAN SYNTHETIC RUBBER CO.,LTD.) 13 August 1997 (1997-08-13) page 43; examples 7,8 ---	1-4,10, 27-29
A	EP 0 473 547 A (CIBA-GEIGY AG) 4 March 1992 (1992-03-04) claims 6,9-11 ---	5-8
A	EP 0 773 478 A (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 14 May 1997 (1997-05-14) page 13, line 1 - line 50 claim 16 -----	5-8

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/25106

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10031310 A	03-02-1998	NONE	
EP 0789278 A	13-08-1997	JP 10111569 A	28-04-1998
EP 0473547 A	04-03-1992	CA 2049772 A	28-02-1992
		JP 4230645 A	19-08-1992
EP 0773478 A	14-05-1997	EP 0877295 A	11-11-1998
		JP 9189998 A	22-07-1997
		US 5928840 A	27-07-1999

## PATENT COOPERATION TREATY

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JAN 30 2001

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PATENT RECORDS  
CENTERFrom the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

MAGEE, Thomas H.  
E.I. DU PONT DE NEMOURS AND COMPANY  
Legal/Patent Records Center  
1007 Market Street  
Wilmington, Delaware 19898  
ETATS-UNIS D'AMERIQUE

JMS

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT  
(PCT Rule 71.1)

Date of mailing  
(day/month/year) 19.01.2001

Applicant's or agent's file reference  
PE0612 PCT

## IMPORTANT NOTIFICATION

International application No.  
PCT/US99/25106

International filing date (day/month/year)  
26/10/1999

Priority date (day/month/year)  
27/10/1998

Applicant  
E.I. DU PONT DE NEMOURS AND COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

## 4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

REY NOTED

Name and mailing address of the IPEA/



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D-80298 Munich  
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Authorized officer

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27 APR 2001

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>PE0612 PCT</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/US99/25106</b>	International filing date ( <i>day/month/year</i> ) <b>26/10/1999</b>	Priority date ( <i>day/month/year</i> ) <b>27/10/1998</b>
International Patent Classification (IPC) or national classification and IPC <b>G03F7</b>		
Applicant <b>E.I. DU PONT DE NEMOURS AND COMPANY et al.</b>		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 8 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I    <input checked="" type="checkbox"/> Basis of the report</li> <li>II   <input type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV   <input type="checkbox"/> Lack of unity of invention</li> <li>V    <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI   <input type="checkbox"/> Certain documents cited</li> <li>VII <input type="checkbox"/> Certain defects in the international application</li> <li>VIII <input checked="" type="checkbox"/> Certain observations on the international application</li> </ul>		
Date of submission of the demand  <b>28/04/2000</b>	Date of completion of this report  <b>19.01.2001</b>	
Name and mailing address of the international preliminary examining authority:   <b>European Patent Office</b> D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  <b>Randez Garcia, F</b>  Telephone No. +49 89 2399 2234	



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/US99/25106

**I. Basis of the report**

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

**Description, pages:**

1,4-19,21-66	as originally filed		
2,2a,3,3a,20	as received on	01/12/2000 with letter of	01/12/2000

**Claims, No.:**

18 (part),19-22	as originally filed		
1-17,18 (part), 23-29	as received on	01/12/2000 with letter of	01/12/2000

**Drawings, sheets:**

1/1	as originally filed
-----	---------------------

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/US99/25106

4. The amendments have resulted in the cancellation of:

- ☐ the description,      pages:
- ☐ the claims,      Nos.:
- ☐ the drawings,      sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims	1-29
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-29
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-29
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/US99/25106

**R It m V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1). The closest prior art is represented by the following documents:

D1: YAMANA M ; ITANI T ; YOSHINO H ; HASHIMOTO S ; TANABE H ;  
KASAMA K: 'Deblocking reaction of chemically amplified ArF positive'  
PROC. SPIE - INT. SOC. OPT. ENG., vol. 3333, no. 1, June 1998 (1998-06),  
pages 32-42, XP002130419 Washington, USA

D2: EP-A-0 473 547 (CIBA-GEIGY AG) 4 March 1992 (1992-03-04)

- 2). D1 discloses chemically amplified, ArF, positive-working photoresists. Among the resists described therein (see fig. 1, particularly compound a), poly(carboxytetracyclododecyl methacrylate<sub>70</sub>-co-tetrahydropyranylcarboxytetracyclododecyl methacrylate<sub>30</sub>) meets all the requirements stated in present claim 1, except that the branch segments are not polymeric and have a number average molecular weight of less than 1000. Therefore, claim 1 is not anticipated by the disclosure of D1. Since process claim 27 is also characterised by this limiting feature, its subject-matter is also novel with regard to D1.
- 3). D2 discloses certain olefinically unsaturated onium salts which can be polymerised and used as photosensitive copolymers in photoresist compositions (see abstract). The photosensitive copolymers represented in claim 6 of D2 by formula (VII) are branch copolymers containing protected acid groups and acid-generating groups. However, they do not meet the requirements specified in present claims 1 and 27 because the branch segments are not polymeric and have a number average molecular weight of less than 1000. Hence, the subject-matter of claims 1 and 27 is not anticipated by D2.



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/US99/25106

- 4). Furthermore, none of D1 and D2 suggests that the pendent moieties containing protected groups should have molecular weights of at least 1000 in order to attain good plasma etch resistance and adhesive properties. Consequently, the subject-matter of claims 1 and 27 involves an inventive step over the prior art considered (Article 33(2) and (3) PCT).
- 5). Claims 2-26 and 28-29 are dependent on claims 1 and 27, respectively. They concern particular embodiments of the new and inventive subject-matter contained in claims 1 and 27 and meet, therefore, the requirements of Article 33(2) and (3) PCT.

**Re Item VIII**

**Certain observations on the international application**

- 6). The description is not in conformity with the claims as required by Rule 5.1(a)(iii) PCT. In particular, some statements on page 4, lines 13 and 19, and page 5, line 15, are not in agreement with the limitation included in claims 1 and 27 concerning a number average molecular weight of at least 1000.

(obtained using an F<sub>2</sub> laser source) may be used for future microelectronics fabrication using 0.100  $\mu\text{m}$  or less design rules. The opacity of traditional UV and deep-UV organic photoresists at 193 nm precludes their use in single-layer schemes at this wavelength. Recently new photoresist compositions comprising cycloolefin-maleic anhydride alternating copolymers have been shown to be useful for imaging of semiconductors at 193 nm (see F. M. Houlihan et al., Macromolecules, **30**, pages 6517-6534 (1997); T. Wallow et al., SPIE, Vol. 2724, pages 355-364; and F. M. Houlihan et al., Journal of Photopolymer Science and Technology, **10**, No. 3, pages 511-520 (1997)).

Comb polymers are a particular class of branched polymers wherein one or more branch (polymer) segments are linked along a linear (polymer) backbone segment. Comb polymers may also be described as linear polymers with polymeric arms. Such polymers typically are prepared by copolymerizing a conventional monomer with a macromer. Macromers are defined by Kawakami in the "Encyclopedia Of Polymer Science And Engineering", Vol. 9, pp. 195-204 (John Wiley & Sons, New York, 1987) to be polymers of molecular weight ranging from several hundred to tens of thousands, with a functional group at the end that can further polymerize, such as an ethylenic, an epoxy, a dicarboxylic acid, a diol or a diamino group. U.S. Patent 5,061,602 discloses the use of such a polymer as a binding agent in a negative-working photopolymerizable material suitable for producing printing forms or resist patterns. The polymer binder disclosed consists of a film-forming copolymer that has a multi-phase morphology where at least one phase has a glass transition temperature below room temperature and at least one other phase has a glass transition temperature above room temperature. The copolymer has an average molecular weight (weight average) of more than 10,000, and is produced using an ethylenically unsaturated macromer with an average molecular weight (weight average) of 1000 to 100,000. The use of graft (comb) copolymers having acid functionality in certain negative-working photosensitive compositions, such as solder masks, has been published (see PCT International Publication No. WO92/15628).

M. Yamana et al., Deblocking Reaction of Chemically Amplified ArF Positive Resists, PROC. SPIE - INT. SOC. OPT. ENG., Vol. 3333, No. 1, pages 32-42 (June 1998) discloses deblocking reaction mechanisms and lithographic performance in chemically amplified positive ArF resists consisting of triphenylsulfonium triflate as an acid generator and the copolymer poly(carboxy-tetracyclododecyl methacrylate<sub>70</sub>-co-tetrahydropyranylcarboxy-tetracyclododecyl methacrylate<sub>30</sub>). EP 0 473 547 A (CIBA-GEIGY AG 4 March 1992) discloses certain olefinically unsaturated onium salts which can be polymerized and used as

photosensitive copolymers in photoresist compositions. The photosensitive copolymers disclosed include branch copolymers containing protected acid groups and acid-generating groups.

5       There is a critical need though for other novel resist compositions for use at 193 nm or lower, and particularly at 157 nm, that have not only high transparency at these short wavelengths but also other suitable key properties, including good plasma etch resistance and adhesive properties. This invention addresses this critical need by providing new advantageous compositions and associated processes, comprising graft (comb) copolymers, which have these key  
10       properties.

### SUMMARY OF THE INVENTION

The present invention comprises:

(A) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight ( $M_n$ ) of at least 1000.

(B) at least one photoacid generator.

In another embodiment, the invention is a positive photoresist as described supra wherein the photoacid generator is covalently bonded to the branched polymer.

The invention also includes a process for preparing a photoresist image on a substrate comprising, in order:

(W) applying a photoresist composition on a substrate, wherein the photoresist composition comprises:

(a) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branched polymer contains sufficient functionality to render the photoresist developable to afford a relief image, upon imagewise exposure to violet or ultraviolet radiation and subsequent heating, and wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight ( $M_n$ ) of at least 1000;

(b) at least one photoacid generator; and

(c) a solvent;

(X) drying the coated photoresist composition to remove solvent and thereby to form a photoresist layer on the substrate;

(Y) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

(Z) developing the exposed photoresist layer having imaged and non-imaged areas to form the relief image on the substrate.

The photoresist compositions of this invention have a particularly good balance of desirable properties, including high transparency to near, far, and extreme ultraviolet light, high plasma etch resistance, and projected high resolution characteristics suitable for microelectronic device fabrication.

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of absorbance ( $\mu\text{m}^{-1}$ ) versus wavelength (nm) in the UV region for corresponding random, block, and graft copolymers having the same or similar comonomer compositions.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)**

Each photosensitive composition of this invention contains a branched polymer, also known as a comb polymer, which contains protected acid groups. The branched polymer has branch segments, known as polymer arms, of limited molecular weight and limited weight ratio relative to a linear backbone segment.

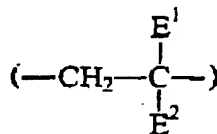
## Process Steps

### Imagewise Exposure

The photoresist compositions of this invention are sensitive in the ultraviolet region of the electromagnetic spectrum and especially to those wavelengths  $\leq 367$  nm. Imagewise exposure of the resist compositions of this invention can be done at many different UV wavelengths including, but not limited to, 365 nm, 248 nm, 193 nm, 157 nm, and lower wavelengths. Imagewise exposure is preferable done with ultraviolet light of 248 nm, 193 nm, 157 nm, or lower wavelengths; is more preferable done with ultraviolet light of 193 nm, 157 nm, or lower wavelengths; and is still more preferably done with ultraviolet light of 157 nm or lower wavelengths. Imagewise exposure can either be done digitally with a laser or equivalent device or non-digitally with use of a photomask. Suitable laser devices for digital imaging of the compositions of this invention include, but are not limited to, an argon-fluorine excimer laser with UV output at 193 nm, a krypton-fluorine excimer laser with UV output at 248 nm, and a fluorine (F2) laser with output at 157 nm. Since, as discussed supra, use of UV light of lower wavelength for imagewise exposure corresponds to higher resolution (lower resolution limit), the use of a lower wavelength (e.g., 193 nm or 157 nm or lower) is generally preferred over use of a higher wavelength (e.g., 248 nm or higher). Specifically, imaging at 157 nm is preferred over imaging at 193 nm for this reason.

### Development

The graft copolymers in the photoresists of this invention must contain sufficient functionality for development following imagewise exposure to UV light. Preferably, the functionality is acid or protected acid such that aqueous development is possible using a basic developer such as sodium hydroxide solution, potassium hydroxide solution, or ammonium hydroxide solution. Some preferred graft copolymers in the resist compositions of this invention are protected acid-containing copolymers comprised of at least one acid-containing monomer of structural unit:



in which  $\text{E}^1$  is H or  $\text{C}_1\text{--C}_{12}$  alkyl;  $\text{E}^2$  is  $\text{CO}_2$ ,  $\text{E}^3$  is  $\text{SO}_3\text{E}$ , or other acidic functional group; and E and  $\text{E}^3$  are H or  $\text{C}_1\text{--C}_{12}$  alkyl, which is unsubstituted or hydroxyl-substituted. Alkyl groups can contain one to twelve carbon atoms and preferably

What is claimed is:

1. A positive-working photoresist comprising:

(A) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight ( $M_n$ ) of at least 1000; and

(B) at least one photoacid generator.

2. The photoresist of Claim 1 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

3. The photoresist of Claim 2 wherein the branch segment(s) contains greater than 50% of the protected acid groups present in the branched polymer.

4. The photoresist of Claim 1 wherein the branched polymer contains functional groups that are compatible with the photoacid generator, said functional groups being distributed in the branched polymer such that 25 to 100% of the functional groups are present in the segment of the branched polymer containing a majority of the protected acid groups.

5. The photoresist of Claim 1 wherein the photoacid generator is covalently bonded to the branched polymer.

6. The photoresist of Claim 5 wherein the photoacid generator is covalently bonded to the branch segment(s).

7. The photoresist of Claim 6 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

8. The photoresist of Claim 7 wherein the branch segment(s) contain greater than 50% of the protected acid groups present in the branched polymer.

9. The photoresist of Claim 1 wherein the branched polymer is comprised of an acrylate polymer, a methacrylate polymer, an acrylate/methacrylate copolymer, and combinations thereof.

10. The photoresist of Claim 1 further comprising a solvent.

11. The photoresist of Claim 1 wherein the branched polymer is formed by addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer.

12. The photoresist of Claim 1 wherein the branched polymer segment is attached to a preformed linear backbone by chemical reaction.

13. The photoresist of Claim 11 wherein

(a) the ethylenically unsaturated macromonomer component has a number average molecular weight ( $M_n$ ) in the range of 1000 to 15,000;

5 (b) the linear backbone segment has a number average molecular weight ( $M_n$ ) between 2,000 and 500,000; and

(c) the weight ratio of the linear backbone segment to the branch segment(s) is within a range of 50/1 to 1/10.

14. The photoresist of Claim 1 wherein the branched polymer has a glass transition temperature of at least 22°C.

10 15. The photoresist of Claim 1 further comprising a dissolution inhibitor.

16. The photoresist of Claim 1 wherein the branched polymer is an acrylic/methacrylic/styrenic copolymer being at least 60% by weight acrylate and having at least 60% of methacrylate repeat units present either in a first location or a second location, the first location being one of the segments, the second location  
15 being a segment different from the first location, wherein at least 60% of the acrylate repeat units are present in the second location.

17. The photoresist of Claim 1 wherein the branched polymer is a fluorine-containing copolymer comprising a repeat unit derived from at least one ethylenically unsaturated compound containing at least one fluorine atom  
20 covalently attached to an ethylenically unsaturated carbon atom.

18. The photoresist of Claim 17 wherein the fluorine-containing copolymer is further comprised of a repeat unit derived from at least one unsaturated compound selected from the group consisting of:



01-12-2000

EP99971104.7

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23. The photoresist of Claim 21 wherein the photoacid generator is covalently bonded to the branched polymer.

24. The photoresist of Claim 23 wherein the photoacid generator is covalently bonded to the branch segment(s).

5 25. The photoresist of Claim 24 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

26. The photoresist of Claim 25 wherein the branch segment(s) contain greater than 50% of the protected acid groups present in the branched polymer.

10 27. A process for preparing a photoresist image on a substrate comprising, in order:

(W) applying a photoresist composition on a substrate, wherein the photoresist composition comprises:

15 (a) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branched polymer contains sufficient functionality to render the photoresist developable to afford a relief image, upon imagewise exposure to radiation selected from the group consisting of ultraviolet and violet and subsequent heating, and wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight  
20 ( $M_n$ ) of at least 1000;

(b) at least one photoacid generator; and

(c) a solvent;

(X) drying the coated photoresist composition to remove solvent and thereby to form a photoresist layer on the substrate;

25 (Y) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

(Z) developing the exposed photoresist layer having images and non-imaged areas to form the relief image on the substrate.

30 28. The process of Claim 27 further comprising a step of heating the photoresist layer following step (X) and prior to step (Z).

29. The process of Claim 27 wherein the photoresist layer is developed with an aqueous alkaline developer.

From the:  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

AUG 31 2000

To:

MAGEE, Thomas H.  
E.I. DU PONT DE NEMOURS AND COMPANY  
Legal/Patent Records Center  
1007 Market Street  
Wilmington, Delaware 19898  
ETATS-UNIS D'AMERIQUE

PCT PATENT RECORDS  
CENTER

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SEP 1 2000  
T. H. MAGEE

WRITTEN OPINION

(PCT Rule 66)

Applicant's or agent's file reference <b>PE0612 PCT</b>		Date of mailing (day/month/year) <b>24.08.2000</b>
International application No. <b>PCT/US99/25106</b>		International filing date (day/month/year) <b>26/10/1999</b>
Priority date (day/month/year) <b>27/10/1998</b>		
International Patent Classification (IPC) or both national classification and IPC <b>G03F7</b>		
Applicant <b>E.I. DU PONT DE NEMOURS AND COMPANY et al.</b>		

- This written opinion is the **first** drawn up by this International Preliminary Examining Authority.
- This opinion contains indications relating to the following items:
  - I ☒ Basis of the opinion
  - II ☐ Priority
  - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV ☐ Lack of unity of invention
  - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☐ Certain document cited
  - VII ☐ Certain defects in the international application
  - VIII ☒ Certain observations on the international application
- The applicant is hereby **invited to reply** to this opinion.
 


**When?** See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

**How?** By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

**Also:** For an additional opportunity to submit amendments, see Rule 66.4. For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis. For an informal communication with the examiner, see Rule 66.6.

**If no reply is filed,** the international preliminary examination report will be established on the basis of this opinion.
- The final date by which the international preliminary examination report must be established according to Rule 69.2 is: **27/02/2001**.

TRB NOTED

Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer / Examiner <b>Randez Garcia, F</b> Formalities officer (incl. extension of time limits) <b>Schuster-Kaechele, W</b> Telephone No. +49 89 2399 2281
---	---



**I. Basis of the opinion**

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*):

**Description, pages:**

1-66 as originally filed

**Claims, No.:**

1-29 as originally filed

**Drawings, sheets:**

1/1 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

3. This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	1-10, 14, 27-29
Inventive step (IS)	Claims	15
Industrial applicability (IA)	Claims	

2. Citations and explanations

**see s parat sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

- 1). Reference is made to the following documents:

D1: YAMANA M ; ITANI T ; YOSHINO H ; HASHIMOTO S ; TANABE H ;  
KASAMA K: 'Deblocking reaction of chemically amplified ArF positive'  
PROC. SPIE - INT. SOC. OPT. ENG., vol. 3333, no. 1, June 1998 (1998-06),  
pages 32-42, XP002130419 Washington, USA

D2: EP-A-0 473 547 (CIBA-GEIGY AG) 4 March 1992 (1992-03-04)

- 2). D1 discloses chemically amplified, ArF, positive-working photoresists. Among the resists described therein (see fig. 1, particularly compound a), poly(carboxytetracyclododecyl methacrylate<sub>70</sub>-co-tetrahydropyranylcboxytetracyclododecyl methacrylate<sub>30</sub>) meets all the requirements stated in present claims 1-4 and 9, which therefore lack novelty.
- 3). Moreover, a process for preparing a photoresist image on a substrate is described on page 33 of D1, item 2-1. Said process meets all the requirements of present claims 27-29, which therefore lack novelty.
- 4). D2 discloses certain olefinically unsaturated onium salts which can be polymerised and used as photosensitive copolymers in photoresist compositions (see abstract). The photosensitive copolymers represented in claim 6 of D2 by formula (VII) are branch copolymers containing protected acid groups and acid-generating groups. Thus, they meet the requirements specified in present claims 5-8.
- 5). Furthermore, D2 discloses that such copolymers may be dissolved in appropriate solvents before coating a substrate to be imaged (see page 8, lines 39-46). Thus, D2 prejudices the patentability of present claim 10.

- 6). Claim 14 is characterised by the Tg of the copolymer. Since the copolymer itself is already known from D1 and/or D2, it must be assumed that the substances disclosed in these documents also has a similar Tg. Therefore, claim 14 would not meet the requirements of Article 33(2) PCT, its subject-matter being not new.
- 7). As for claim 15, the addition of a dissolution inhibitor is a very well-known feature in the art of positive-working photoresists. In the absence of an unexpected technical effect, this feature does not contribute to the necessary inventive step. Therefore, the subject-matter claim 15 cannot be considered as being inventive.

**Re Item VIII**

**Certain observations on the international application**

- 8). Claim 13 seems to contain a typographical error. The back reference to claim 1 should probably point to claim 11, since it is in the latter claim where the macromer component of claim 13, item (a), is mentioned for the first time.
- 9). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1 and D2 is not mentioned in the description, nor are these documents identified therein.
- 10). The applicant is requested to file amendments by way of replacement pages in the manner stipulated by Rule 66.8(a) PCT. In particular, fair copies of the amendments should be filed preferably in triplicate.

(obtained using an F<sub>2</sub> laser source) may be used for future microelectronics fabrication using 0.100 µm or less design rules. The opacity of traditional UV and deep-UV organic photoresists at 193 nm precludes their use in single-layer schemes at this wavelength. Recently new photoresist compositions comprising cycloolefin-maleic anhydride alternating copolymers have been shown to be useful for imaging of semiconductors at 193 nm (see F. M. Houlihan et al., Macromolecules, **30**, pages 6517-6534 (1997); T. Wallow et al., SPIE, Vol. 2724, pages 355-364; and F. M. Houlihan et al., Journal of Photopolymer Science and Technology, **10**, No. 3, pages 511-520 (1997)).

Comb polymers are a particular class of branched polymers wherein one or more branch (polymer) segments are linked along a linear (polymer) backbone segment. Comb polymers may also be described as linear polymers with polymeric arms. Such polymers typically are prepared by copolymerizing a conventional monomer with a macromer. Macromers are defined by Kawakami in the "Encyclopedia Of Polymer Science And Engineering", Vol. 9, pp. 195-204 (John Wiley & Sons, New York, 1987) to be polymers of molecular weight ranging from several hundred to tens of thousands, with a functional group at the end that can further polymerize, such as an ethylenic, an epoxy, a dicarboxylic acid, a diol or a diamino group. U.S. Patent 5,061,602 discloses the use of such a polymer as a binding agent in a negative-working photopolymerizable material suitable for producing printing forms or resist patterns. The polymer binder disclosed consists of a film-forming copolymer that has a multi-phase morphology where at least one phase has a glass transition temperature below room temperature and at least one other phase has a glass transition temperature above room temperature. The copolymer has an average molecular weight (weight average) of more than 10,000, and is produced using an ethylenically unsaturated macromer with an average molecular weight (weight average) of 1000 to 100,000. The use of graft (comb) copolymers having acid functionality in certain negative-working photosensitive compositions, such as solder masks, has been published (see PCT International Publication No. WO92/15628).

There is a critical need though for other novel resist compositions for use at 193 nm or lower, and particularly at 157 nm, that have not only high transparency at these short wavelengths but also other suitable key properties, including good plasma etch resistance and adhesive properties. This invention addresses this critical need by providing new advantageous compositions and associated processes, comprising graft (comb) copolymers, which have these key properties.

### SUMMARY OF THE INVENTION

The present invention comprises:

(A) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear

5 backbone segment; and

(B) at least one photoacid generator.

In another embodiment, the invention is a positive photoresist as described supra wherein the photoacid generator is covalently bonded to the branched polymer.

The invention also includes a process for preparing a photoresist image on a  
10 substrate comprising, in order:

(W) applying a photoresist composition on a substrate, wherein the photoresist composition comprises:

(a) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a  
15 linear backbone segment, wherein the branched polymer contains sufficient functionality to render the photoresist developable to afford a relief image, upon imagewise exposure to violet or ultraviolet radiation and subsequent heating;

(b) at least one photoacid generator; and

(c) a solvent;

20 (X) drying the coated photoresist composition to remove solvent and thereby to form a photoresist layer on the substrate;

(Y) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

25 (Z) developing the exposed photoresist layer having imaged and non-imaged areas to form the relief image on the substrate.

The photoresist compositions of this invention have a particularly good balance of desirable properties, including high transparency to near, far, and extreme ultraviolet light, high plasma etch resistance, and projected high resolution characteristics suitable for microelectronic device fabrication.

### BRIEF DESCRIPTION OF THE DRAWINGS

30 Figure 1 is a plot of absorbance ( $\mu\text{m}^{-1}$ ) versus wavelength (nm) in the UV region for corresponding random, block, and graft copolymers having the same or similar comonomer compositions.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

35 Each photosensitive composition of this invention contains a branched polymer, also known as a comb polymer, which contains protected acid groups. The branched polymer has branch segments, known as polymer arms, of limited molecular weight and limited weight ratio relative to a linear backbone segment.

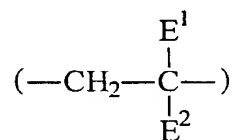


Process StepsImagewise Exposure

The photoresist compositions of this invention are sensitive in the ultraviolet region of the electromagnetic spectrum and especially to those wavelengths  $\leq 367$  nm. Imagewise exposure of the resist compositions of this invention can be done at many different UV wavelengths including, but not limited to, 365 nm, 248 nm, 193 nm, 157 nm, and lower wavelengths. Imagewise exposure is preferable done with ultraviolet light of 248 nm, 193 nm, 157 nm, or lower wavelengths; is more preferable done with ultraviolet light of 193 nm, 157 nm, or lower wavelengths; and is still more preferably done with ultraviolet light of 157 nm or lower wavelengths. Imagewise exposure can either be done digitally with a laser or equivalent device or non-digitally with use of a photomask. Digital imaging with a laser is preferred. Suitable laser devices for digital imaging of the compositions of this invention include, but are not limited to, an argon-fluorine excimer laser with UV output at 193 nm, a krypton-fluorine excimer laser with UV output at 248 nm, and a fluorine (F<sub>2</sub>) laser with output at 157 nm. Since, as discussed supra, use of UV light of lower wavelength for imagewise exposure corresponds to higher resolution (lower resolution limit), the use of a lower wavelength (e.g., 193 nm or 157 nm or lower) is generally preferred over use of a higher wavelength (e.g., 248 nm or higher). Specifically, imaging at 157 nm is preferred over imaging at 193 nm for this reason.

Development

The graft copolymers in the photoresists of this invention must contain sufficient functionality for development following imagewise exposure to UV light. Preferably, the functionality is acid or protected acid such that aqueous development is possible using a basic developer such as sodium hydroxide solution, potassium hydroxide solution, or ammonium hydroxide solution. Some preferred graft copolymers in the resist compositions of this invention are protected acid-containing copolymers comprised of at least one acid-containing monomer of structural unit:



in which E<sup>1</sup> is H or C<sub>1</sub>-C<sub>12</sub> alkyl; E<sup>2</sup> is CO<sub>2</sub>, E<sup>3</sup> is SO<sub>3</sub>E, or other acidic functional group; and E and E<sup>3</sup> are H or C<sub>1</sub>-C<sub>12</sub> alkyl, which is unsubstituted or hydroxyl-substituted. Alkyl groups can contain one to twelve carbon atoms and preferably

What is claimed is:

1. A positive-working photoresist comprising:
  - (A) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment; and
  - (B) at least one photoacid generator.
2. The photoresist of Claim 1 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.
3. The photoresist of Claim 2 wherein the branch segment(s) contains greater than 50% of the protected acid groups present in the branched polymer.
4. The photoresist of Claim 1 wherein the branched polymer contains functional groups that are compatible with the photoacid generator, said functional groups being distributed in the branched polymer such that 25 to 100% of the functional groups are present in the segment of the branched polymer containing a majority of the protected acid groups.
5. The photoresist of Claim 1 wherein the photoacid generator is covalently bonded to the branched polymer.
6. The photoresist of Claim 5 wherein the photoacid generator is covalently bonded to the branch segment(s).
7. The photoresist of Claim 6 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.
8. The photoresist of Claim 7 wherein the branch segment(s) contain greater than 50% of the protected acid groups present in the branched polymer.
9. The photoresist of Claim 1 wherein the branched polymer is comprised of an acrylate polymer, a methacrylate polymer, an acrylate/methacrylate copolymer, and combinations thereof.
10. The photoresist of Claim 1 further comprising a solvent.
11. The photoresist of Claim 1 wherein the branched polymer is formed by addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer.
12. The photoresist of Claim 1 wherein the branched polymer segment is attached to a preformed linear backbone by chemical reaction.

13. The photoresist of Claim 1 wherein

- (a) the ethylenically unsaturated macromer component has a number average molecular weight ( $M_n$ ) in the range of 500 to 40,000;
- 5 (b) the linear backbone segment has a number average molecular weight ( $M_n$ ) between about 2,000 and about 500,000; and
- (c) the weight ratio of the linear backbone segment to the branch segment(s) is within a range of about 50/1 to about  
10 1/10.

14. The photoresist of Claim 1 wherein the branched polymer has a glass transition temperature of at least 22°C.

15. The photoresist of Claim 1 further comprising a dissolution inhibitor.

16. The photoresist of Claim 1 wherein the branched polymer is an  
15 acrylic/methacrylic/styrenic copolymer being at least 60% by weight acrylate and having at least 60% of methacrylate repeat units present either in a first location or a second location, the first location being one of the segments, the second location being a segment different from the first location, wherein at least 60% of the acrylate repeat units are present in the second location.

20 17. The photoresist of Claim 1 wherein the branched polymer is a fluorine-containing copolymer comprising a repeat unit derived from at least one ethylenically unsaturated compound containing at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom.

25 18. The photoresist of Claim 17 wherein the fluorine-containing copolymer is further comprised of a repeat unit derived from at least one unsaturated compound selected from the group consisting of:

23. The photoresist of Claim 21 wherein the photoacid generator is covalently bonded to the branched polymer.

24. The photoresist of Claim 23 wherein the photoacid generator is covalently bonded to the branch segment(s).

5        25. The photoresist of Claim 24 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

26. The photoresist of Claim 25 wherein the branch segment(s) contain greater than 50% of the protected acid groups present in the branched polymer.

10       27. A process for preparing a photoresist image on a substrate comprising, in order:

(W) applying a photoresist composition on a substrate, wherein the photoresist composition comprises:

15       (a) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branched polymer contains sufficient functionality to render the photoresist developable to afford a relief image, upon imagewise exposure to radiation selected from the group consisting of ultraviolet and violet and subsequent heating;

20       (b) at least one photoacid generator; and

(c) a solvent;

(X) drying the coated photoresist composition to remove solvent and thereby to form a photoresist layer on the substrate;

(Y) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

25       (Z) developing the exposed photoresist layer having imaged and non-imaged areas to form the relief image on the substrate.

28. The process of Claim 27 further comprising a step of heating the photoresist layer following step (X) and prior to step (Z).

30       29. The process of Claim 27 wherein the photoresist layer is developed with an aqueous alkaline developer.

# PATENT COOPERATION TREATY

## PCT

REC'D 24 JAN 2001

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

15

Applicant's or agent's file reference PE0612 PCT		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US99/25106	International filing date (day/month/year) 26/10/1999	Priority date (day/month/year) 27/10/1998
International Patent Classification (IPC) or national classification and IPC G03F7		
Applicant E.I. DU PONT DE NEMOURS AND COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  28/04/2000	Date of completion of this report  19.01.2001
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Randez Garcia, F  Telephone No. +49 89 2399 2234



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US99/25106

## I. Basis of this report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

### Description, pages:

1,4-19,21-66	as originally filed		
2,2a,3,3a,20	as received on	01/12/2000 with letter of	01/12/2000

### Claims, No.:

18 (part),19-22	as originally filed		
1-17,18 (part), 23-29	as received on	01/12/2000 with letter of	01/12/2000

### Drawings, sheets:

1/1	as originally filed
-----	---------------------

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US99/25106

4. The amendments have resulted in the cancellation of:

- ☐ the description,      pages:
- ☐ the claims,      Nos.:
- ☐ the drawings,      sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims	1-29
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-29
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-29
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**R I t m V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

- 1). The closest prior art is represented by the following documents:

D1: YAMANA M ; ITANI T ; YOSHINO H ; HASHIMOTO S ; TANABE H ;  
KASAMA K: 'Deblocking reaction of chemically amplified ArF positive'  
PROC. SPIE - INT. SOC. OPT. ENG., vol. 3333, no. 1, June 1998 (1998-06),  
pages 32-42, XP002130419 Washington, USA

D2: EP-A-0 473 547 (CIBA-GEIGY AG) 4 March 1992 (1992-03-04)

- 2). D1 discloses chemically amplified, ArF, positive-working photoresists. Among the resists described therein (see fig. 1, particularly compound a), poly(carboxytetracyclododecyl methacrylate<sub>70</sub>-co-tetrahydropyranylcarboxytetracyclododecyl methacrylate<sub>30</sub>) meets all the requirements stated in present claim 1, except that the branch segments are not polymeric and have a number average molecular weight of less than 1000. Therefore, claim 1 is not anticipated by the disclosure of D1. Since process claim 27 is also characterised by this limiting feature, its subject-matter is also novel with regard to D1.
- 3). D2 discloses certain olefinically unsaturated onium salts which can be polymerised and used as photosensitive copolymers in photoresist compositions (see abstract). The photosensitive copolymers represented in claim 6 of D2 by formula (VII) are branch copolymers containing protected acid groups and acid-generating groups. However, they do not meet the requirements specified in present claims 1 and 27 because the branch segments are not polymeric and have a number average molecular weight of less than 1000. Hence, the subject-matter of claims 1 and 27 is not anticipated by D2.



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/US99/25106

- 4). Furthermore, none of D1 and D2 suggests that the pendent moieties containing protected groups should have molecular weights of at least 1000 in order to attain good plasma etch resistance and adhesive properties. Consequently, the subject-matter of claims 1 and 27 involves an inventive step over the prior art considered (Article 33(2) and (3) PCT).
- 5). Claims 2-26 and 28-29 are dependent on claims 1 and 27, respectively. They concern particular embodiments of the new and inventive subject-matter contained in claims 1 and 27 and meet, therefore, the requirements of Article 33(2) and (3) PCT.

**Re Item VIII**

**Certain observations on the international application**

- 6). The description is not in conformity with the claims as required by Rule 5.1(a)(iii) PCT. In particular, some statements on page 4, lines 13 and 19, and page 5, line 15, are not in agreement with the limitation included in claims 1 and 27 concerning a number average molecular weight of at least 1000.

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>PE0612 PCT</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/US 99/ 25106</b>	International filing date (day/month/year) <b>26/10/1999</b>	(Earliest) Priority Date (day/month/year) <b>27/10/1998</b>
Applicant <b>E. I. DU PONT DE NEMOURS AND COMPANY et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 5 sheets.  
☒ It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1 (b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☒ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

### 4. With regard to the **title**,

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established by this Authority to read as follows:

### 5. With regard to the **abstract**,

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

- ☒ as suggested by the applicant.
- ☐ because the applicant failed to suggest a figure.
- ☐ because this figure better characterizes the invention.

01

☐ None of the figures.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 99/25106

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 2.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

**1. Claims: 1-4, 9-29**

A positive-working photoresist comprising:  
(A) a branched polymer containing protected acids, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment; and  
(B) at least one photoacid generator

**2. Claims: 5-8**

A positive-working photoresist comprising a branched polymer containing (a) protected acids, (b) one or more branch segment(s) chemically linked along a linear backbone segment, and (c) a photoacid generator covalently bonded to the branched polymer

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/25106

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03F7/039 G03F7/004

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YAMANA M ; ITANI T ; YOSHINO H ; HASHIMOTO S ; TANABE H ; KASAMA K: "Deblocking reaction of chemically amplified ArF positive" PROC. SPIE - INT. SOC. OPT. ENG., vol. 3333, no. 1, June 1998 (1998-06), pages 32-42, XP002130419 Washington, USA page 33 page 37; figure 1 --- -/-	1-4,9, 10,27-29

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## ° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

29 June 2000

Date of mailing of the international search report

07. 07. 2000

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/25106

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199815 Derwent Publications Ltd., London, GB; Class A89, AN 1998-164829 XP002130420 & JP 10 031310 A (NIPPON GOSEI GOMU KK), 3 February 1998 (1998-02-03) abstract ---	1-4,10, 27-29
X	EP 0 789 278 A (JAPAN SYNTHETIC RUBBER CO.,LTD.) 13 August 1997 (1997-08-13) page 43; examples 7,8 ---	1-4,10, 27-29
A	EP 0 473 547 A (CIBA-GEIGY AG) 4 March 1992 (1992-03-04) claims 6,9-11 ---	5-8
A	EP 0 773 478 A (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 14 May 1997 (1997-05-14) page 13, line 1 - line 50 claim 16 -----	5-8

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/25106

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10031310 A	03-02-1998	NONE	
EP 0789278 A	13-08-1997	JP 10111569 A	28-04-1998
EP 0473547 A	04-03-1992	CA 2049772 A	28-02-1992
		JP 4230645 A	19-08-1992
EP 0773478 A	14-05-1997	EP 0877295 A	11-11-1998
		JP 9189998 A	22-07-1997
		US 5928840 A	27-07-1999